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# METHOD FOR PURIFYING ANTHOCYANIN DYESTUFF
[Shikiso antoshianin no seiseiho]

Kinnosuke Kotake, et al.

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| INVENTORS | (72): | KOTAKE, KINNOSUKE; YASUDA, AKIRA; OBATA, MASAHIKO |
| APPLICANT | (71): | SANEI KAGAKU KOGYO K.K. |
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Specifications

1. Title of the Invention

METHOD FOR PURIFYING ANTHOCYANIN DYESTUFF

2. Claim(s)

(1) A purification method characterized by removing fat, starch, pulp, and the like from an anthocyanin aqueous solution, alcohol solution, and the like during purification of anthocyanin by using a cation exchange resin, then subjecting it to an ultrafiltration membrane treatment, removing solute molecules having a molecular weight of about 20,000 or greater in the residual cross-substances, and further, adding a silica gel and/or treating it under reduced pressure.

(2) The method of Claim (1) in which the silica gel is added to the system after the cation exchange resin treatment and/or reduced-pressure treatment.

3. Detailed Specifications

(Field of Industrial Application)

This invention pertains to an anthocyanin dyestuff for food products, and in particular, an edible anthocyanin dyestuff. Anthocyanin is a red or reddish purple dyestuff, and it is water-soluble.

(Prior Art)

Purifying plants containing anthocyanin, such as red cabbage, red grape peelings, berries, purple corn, and their aqueous solutions or alcohol extracts, using centrifugal separation, decantation filtration, an ion exchange resin, and the like, is the method performed generally in the past.

However, finished goods having high purity cannot be obtained in such a method. The reason for that is because the fat, starch, fine pulp, water-soluble protein, polysaccharide, and the like contained in the raw material anthocyanin extract are difficult to remove. The presence of cross-products of these cause malodors that greatly adversely affect, e.g., the brightness and chromacity of the resulting substance, even in tiny amounts.

(Problems to be Solved by the Invention)

It is an object to industrially and effectively obtain anthocyanin free of malodors and excellent in brightness and chromacity without producing any precipitates over time in a colored solution by eliminating the drawbacks of the conventional method.

(Means for Solving the Problems)

First of all, a solution, such as an anthocyanin aqueous solution or alcohol solution, is defined as the object. Such an anthocyanin solution is obtained from an anthocyanin-containing plant as in the conventional method. In order to enhance the dye-extracting effect in this case, the pH of the system is usually provided as an acidic system.

By cloth filtration, centrifugal separation or other methods, a residue in which the crude cross-substances have been removed therefrom is defined as the starting material for the next step.

Starch, saccharide, fat, bulky pulp, and the like contained in the starting material are adsorbed with this resin, and the adsorbed material is removed. In this case, the pH of the system is preferably 4.0 or less to increase anthocyanin yield. Then, the liquid residue is applied to

an ultrafiltration membrane treatment step. The pH of this liquid system is preferably set to 4 or less. By doing this, the system solvent and the small solute molecules filter through this membrane, but the large solute particles are impossible to filter therethrough. A molecular weight of about 20,000 serves as the criteria for judging the size of the solute molecules herein. By doing this, large solute molecules (pulp) of about 20,000 or higher cannot be contained substantially in the liquid dyestuff.

ACV-3050 of Asahi Chemical Industry Co., Ltd., NTN-3510 and NTN-4220 of Nitto Denko Corp., DMH 250 of Daicel Chemical Industries, Ltd., and the like are cited as examples of the ultrafiltration membrane being used. Then, a silica gel is added to the resulting liquid dyestuff to obtain a homogenous solution system. This treatment may be performed by reducing the pressure of the system. The complete disappearance of the malodors in the liquid is limited with the amount of use thereof or the reduced-pressure treatment limits. The temperature of the system is optional, but in order to minimize the amount of destruction of the contained dyestuff, it is more preferable that it be set at a temperature of room temperature or less. This step may be performed before or during the ultrafiltration membrane step.

The resulting liquid coloring is the target anthocyanin dyestuff, which can be made into the form of a concentrated solution or a dried powder. Moreover, in order to eliminate malodors, it is apparent that the reduced-pressure treatment may be performed on such a concentrated liquid or dried powder. This object can be achieved in this invention herein.

(Effects)

a. Due to the cation exchange resin treatment in the 1st step, fat, starch, bulk pulp, and the like in the target liquid dyestuff are removed in a practical manner.

b. Due to the ultrafiltration membrane treatment in the 2nd step, the cross-substances in the liquid dyestuff having a solute molecular weight of about 20,000 or more are removed.

c. In the two 2 steps above, the treatments cannot be performed in a sequence in which the ultrafiltration membrane treatment is performed first and the cation exchange resin treatment after that, in reverse to the above-mentioned sequence. The particulars thereof will be described in the test example next.

(Test Example)

(Table) Sequence of Treatment Steps and Effects Thereof

| Test | | A | B | C | D | E | F |
|---|---|---|---|---|---|---|---|
| Cation exchange resin adsorption | Daiaion WK-10 8V=2 | 1 | 1 | 2 | 3 | 3 | 2 |
| Ultrafiltration membrane | NTU-4220 7 $kg/cm^2$ | 2 | 3 | 1 | 1 | 2 | 3 |
| Silica gel | 1.0% | 3 | 2 | 3 | 2 | 1 | 1 |
| Evaluation | Turbidity | 0.001 | 0.001 | 0.007 | 0.006 | 0.006 | 0.002 |
| | Dregs | ○ | ○ | × | × | × | ○ |
| | Odor | ○ | ○ | ○ | ○ | ○ | ○ |

Notes) Turbidity: An OD of 700 mm is exhibited with a drink containing 5% grape juice when the dyestuff is added at an OD max×0.8.

d. The malodorous constituents are removed by means of the silica gel and/or by the reduced-pressure treatment.

This invention is described in detail next with reference to the practical examples.

Practical Example 1

1,000 L of a red cabbage liquid dyestuff extract (L=66.5; a=55.0; b=-9.3; $E^{10\%}_{1\ cm}$=1.5; pH: 2.5; ethanol: 10%; turbidity: 0.051) was passed through 10 L of Daiaion WK-10 at 20°C and SV-3 to obtain a liquid dyestuff excepting polysaccharides, proteins, etc. (L=66.8; a=56.6; b=-9.8; $E^{10\%}_{1\ cm}$=1.4; pH: 2.5; ethanol: 10%; turbidity: 0.082)

Silica gel (500 g) was added to this liquid dyestuff and an approximately 3-hour filtration under stirring and deodorization were performed at 25°C. In this treatment, 1,200 L of a deodorized liquid dyestuff was obtained (L=66.4; a=54.3; d=-9.0; $E^{10\%}_{1\ cm}$=1.0; pH: 2.5; ethanol: 10%; turbidity: 0.021).

Next, filtration was performed at a flow rate of 18 L/min and at 26°C with 7 kg/cm$^2$ of NTV-35100 ultrafiltration membrane made by Nitto Denko Corp. In this case, a 10% alcohol solution (2,000 L) of 0.1% citric acid (molecular weight: 100,000 cut) was added gradually to obtain 2,800 L of a filtrate (L=66.6; a=55.2; b=-9.1; $E^{10\%}_{1\ cm}$=0.32; pH: 2.5; ethanol: 10%; turbidity: 0.001).

20 kg/cm$^2$ of this dyestuff filtrate was concentrated at 25°C and a flow rate of 5L/min with a reverse osmosis membrane (NTR-7250, made by Nitto Denko Corp.) to obtain a concentrated liquid dyestuff (L=66.7; a=56.3; b=-9.6; $E^{10\%}_{1\ cm}$=80; pH: 2.3; 11.2 kg; turbidity: 0.002). Upon preparing a fruit drink with this purified liquid dyestuff (12% sugar, 5% grape juice, 0.2% citric acid, 0.1% liquid dyestuff), mostly a white precipitate developed on the second day, and when stored at 38°C, whereas a faint malodor developed at day 14, no occurrence of either precipitation

or malodors was recognized.

Practical Example 2

A filtration was performed with a Daicel Chemical Industries, Ltd. ultrafiltration membrane, DMH20, by adding a 0.5% silica gel to a liquid dyestuff in which 1,000 L of an elderberry extract liquid dyestuff (L=58.5; a=42.8; b=10.7; $E^{10\%}{}_{1\ cm}$=20; pH: 1.8; turbidity: 0.04) was passed through a Duolite C-464 cation exchange resin at SV=1. The ultrafiltration was performed at conditions including an average 5 kg/cm$^2$, 30°C, and a flow rate of 10 L/min. 4,000 L of a transparent liquid (L=58.4; a=42.6; b=10.8; $E^{10\%}{}_{1\ cm}$: 3.3; pH: 2.0; turbidity: 0.0017). This treatment solution was concentrated by a vacuum concentrator to obtain 100 kg concentrated liquid dyestuff (L=58.6; a=42.8; b=10.6; $E^{10\%}{}_{1\ cm}$=130; pH: 2.6; turbidity: 0.0001) 30 kg of an excipient, dextrin, were added, and dried by a vacuum freeze-dryer to obtain 60 kg dyestuff powder (L=58.5; a=42.7; b=10.7; $E^{10\%}{}_{1\ cm}$=180; pH: 2.5; turbidity: 0.0001).

Upon preparing a fruit drink with this purified powder dyestuff, no occurrence of precipitation, malodors, and the like, as with conventional products, was recognized during storage for one 1 month at 5 to 10°C and at 38°C.

Example 3

5 kg silica gel were added to 1,000 L of a purple corn liquid dyestuff extract (L=67.5; a=44.5; b=19.6; $E^{10\%}{}_{1\ cm}$=15.0; pH: 2.8; turbidity: 0.043), stirred for 2 hours and subsequently filtered with silica gel to obtain 1,000 L of a deodorized liquid dyestuff ($E^{10\%}{}_{1\ cm}$=14.8; pH: 2.8; turbidity: 0.043). Then this was subjected to a deproteinization treatment through

50 L of a cation exchange resin, Daiaion WK-20, at 20°C and SV=1 to obtain 1,200 L (L=66.6; a=45.3; b=20.5; $E^{10\%}_{1\ cm}$=11.8; pH: 2.9; turbidity: 0.013).

This treated liquid dyestuff was treated with an Asahi Chemical Industry Co., Ltd. ultrafiltration membrane, ACV-3050, at conditions of 25 to 30°C and 2 kg/cm$^2$ to obtain 1,500 L of an ultrafiltrate (L=66.6; a=45.1; b=19.2; $E^{10\%}_{1\ cm}$=5.0; pH: 3.0; turbidity: 0.001).

This treated liquid dyestuff was concentrated in a vacuum to prepare 90 kg of a concentrated liquid dyestuff (L=67.4; a=44.5; b=20.4; $F^{10\%}_{1\ cm}$:80; pH: 2.3; turbidity: 0.002). Upon preparing a fruit drink with this liquid dyestuff, no occurrence of the dregs or malodors seen in the past were recognized even at one 1 month at 38° C and one 1 month at 5 to 10°C.

(Advantages of the Invention)

Anthocyanin outstanding in brightness and chromacity with no malodors can be obtained industrially and effectively.